

REMARKS/ARGUMENTS

The claims remain as 1-7, 9, 11-13, 15 and 17-35.

Examiner Zimmer is thanked for the interview courteously granted Applicants' undersigned representative on February 9, 2006. The following includes the substance of the presentation made at that interview.

The specification is amended, in regard to the specification of the polysiloxane molecular weight, by inserting a paragraph indicating that by "molecular weight" Applicants intend "number average molecular weight", which is the molecular weight in the usual classical sense or the ordinary average molecular weight usually meant. In support thereof, Applicants refer to the text, "*Principles of High-Polymer Theory and Practice*", Schmidt and Marlies, McGraw Hill, 1948, pages 8 and 238, copies attached.

The claims, where appropriate, that is Claims 1, 2, 3 and 31, are amended to state expressly that the molecular weight intended is the "number average" molecular weight.

Re The Detailed Action

Reconsideration and withdrawal of the rejection of Claims 1-7, 9-13, 15, 17-29, 31, and 34-35 under 35 U.S.C. § 112, first paragraph, as failing to comply with the enablement requirement are requested.

The focus of the issue is stated as follows in the Official Action.

As before, the original disclosure doesn't provide any indication as to whether it is number-average or weight-average molecular weight that is being recited.

Applicants respond by referring to the statements in the textbook *Principles of High-Polymer Theory and Practice*, Schmidt and Marlies, McGraw-Hill, 1948, pages 7, 8, 237 and 238 wherein it is stated, referring to high polymers on page 8, that " \overline{M}_n " is the molecular

weight in the usual classical sense” and on page 238, that “number-average molecular weight is the ordinary average molecular weight usually meant”.

Accordingly, Applicants submit that their position that by reciting “molecular weight higher than 500,000”, referring to the polysiloxane polymer, (page 3, lines 11 to 13), one skilled in the art would understand that the number average molecular weight is identified and therefore, it is Applicants’ position that the application disclosure and the claims based thereon comply with the enablement requirement.

The MPEP, 8th ed. Rev. 3, Aug. 2005 at page 2100-191 in section 2163.07 states, under the heading “Obvious Errors”,

An amendment to correct an obvious error does not constitute new matter where one skilled in the art would not only recognize the existence of error in the specification, but also the appropriate correction. *in re Odd*, (sic, Oda) 443 F.2d 1200, 170 USPQ 268 (CCPA 1971).

In the cited case of In re Oda, (copy enclosed) the court quotes from the case of *Quigley v. Zimmerman*, 73 F.2d 499, 23 USPQ 310 (CCPA 1934), wherein the court stated:

That amendments may be made to patent applications for the purpose of *curing defects, obvious to one skilled in the art*, in the drawings or written descriptions of inventions, is so well settled that we deem it unnecessary to cite authorities in support thereof.

It would appear therefore that the asserted defect is appropriately cured by the amendment here presented.

The copies of publications of record would appear to support Applicants’ position. The two previously submitted Dow Corning® product description print-outs, Dow Corning® 200(R) Fluid 60,000 CST and Dow Corning® 200(R) Fluid 300,000 CST identify average molecular weights of 95,000 and 204,000, without identifying the type. Page 934 of the Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., 1982, relates number average molecular weight to viscosity of dimethyl silicone polymers. In U.S. Patent 6,849,265,

referred to during a previous telephonic interview (please see the Examiner-initiated Interview Summary dated 30 November 2005), which patent is assigned to the General Electric Co., a producer in the polysiloxane or silicone field, it is stated that, referring to a component of the disclosed composition:

The polysiloxane or silicone resin typically has a molecular weight in a range between about 100 and about 6,000,000, preferably in a range between about 250 and about 50,000, more preferably in a range between about 500 and about 25,000, and most preferably in a range between about 500 and about 15,000.

The type of molecular weight average intended is not specifically identified.

In the herewith submitted copy page 936 of Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 20, 1982, there appears the statement relating to the production of high viscosity gums or fluids with the use of alkaline catalysts

Polymerization is continued in the case of gums to make polymers of >500,000 av mol wt and 10^7 mm²/s(=cSt) viscosity.

Again, no identification of the type of molecular weight average appears.

And, finally, in the herewith submitted article by Grubb & Osthoff, J. Amer. Chem. Soc. Vol. 77, 1955, pg. 1405, number average molecular weights of the high polymers produced are recorded, these being over 10^6 after only 10% conversion, please see Table V, pg. 1408 and the succeeding paragraph.

It is evident therefore that molecular weights are reported as number average molecular weights in this field and reference to "molecular weight" without more should be construed in this field as reference to "number average molecular weight".

Reconsideration and withdrawal of the rejection of Claim 30 under 35 U.S.C. § 102(b) as being anticipated by Tanaka et al., U.S. Patent No. 5,416,151 are also requested.

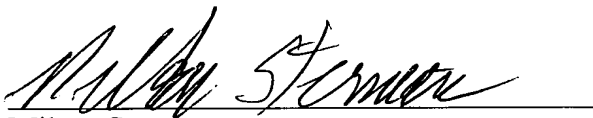
Claim 30 does in fact recite a broader range of proportions of 0.01 to 10 wt.%. However, the polymers itemized in Claim 30, for which basis exists at page 6, the paragraph at line 5, are all polar organic polymers, none of which are disclosed or suggested by Tanaka et al. The patentees' invention relates to a poly 1-butene resin admixed with a filler and hydrocarbonic oil. Further, though the Tanaka composition may contain an additional thermoplastic resinous component (D), that component is another hydrocarbon polymer as disclosed at col. 4, the paragraph at line 22. It is not one of the polymers listed in Claim 30.

Hence, Applicants submit that there is no anticipation.

Favorable reconsideration is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.
Norman F. Oblon



Milton Serman
Registration No. 27,499

Customer Number
22850

Tel: (703) 413-3000
Fax: (703) 413 -2220
(OSMMN 06/04)

ENGINEERING SERIES

by the Following Committee

ET E. MARSHALL · President, Rumford
Chemical Works

McBRIDE · Consulting Chemical Engineer

A. STINE · Director, E. I. du Pont de
Moures & Co.

WEIDLEIN · Director, Mellon Institute of
Industrial Research

WHITAKER · Director, American Cyan-
amid Company

WHITE · Professor Emeritus of Chemical
Engineering, University of Michigan

ER G. WHITMAN · Professor of Chem-
ical Engineering, Massachusetts Institute of
Technology

ES

nology

Engineering

ulations

s

inum. Industry (in Two Volumes):
Products and Their Fabrication

ils

ok

Supervision

Measurement and Control

Polymer Theory and Practice

Chemical Engineering

1

Principles of Chemical Engineering
Practice

Principles of HIGH-POLYMER THEORY AND PRACTICE

FIBERS · PLASTICS · RUBBERS · COATINGS · ADHESIVES

by ALOIS X. SCHMIDT

Assistant Professor in Chemical Engineering
College of the City of New York

and CHARLES A. MARLIES

Associate Professor in Chemical Engineering
College of the City of New York

FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.

NEW YORK TORONTO LONDON

1948

itself difficult, the molecules in the polymerization process they do not produce a product is devoid of precise molecular weight, it is impossible to purify, distill, or separate the components by weight, sorption of impurities are exactly alike. For these reasons, the only thing they could do—scribbling in their notebooks and making statements of indefinite character was

on high polymers therefore requiring the application of the techniques as well as the development of new analysis.

Carothers, Flory, Huggins, and others of the main obstacles in the way of polymer science. In the following decade, the development of reaction mechanisms made it possible to select fairly accurately the conditions to produce a high polymer with a

which may be built up, so also may be effected by any process whereby degradation is called *depolymerization* and monomers are recovered.

It may be effected by thermal or by chemical means (of condensation polymers). There is evidence that mechanical working.

With the high polymer ready to use, it is at its maximum degree of stability. If it is subsequently subjected to degradation, it is undesirable. At other times it is developed to control it lest it be degraded, deliberate degradation is a process employed in the

of polymers. It has already been pointed out that not all the molecules of a polymer are usually more or less the same size and molecular

weights of individual molecules. Figure 1-2 shows the size-distribution curves for several polymers. (Molecular-weight distribution is discussed in Secs. 407 ff. and Sec. 614.)

It is well to bear in mind from the very beginning that a high-polymer mass, no matter how "pure," does not possess a molecular weight in the usual sense. Rather, it has an *average* molecular weight. Furthermore, when one refers to the degree of polymerization, one means the *average* degree of polymerization.

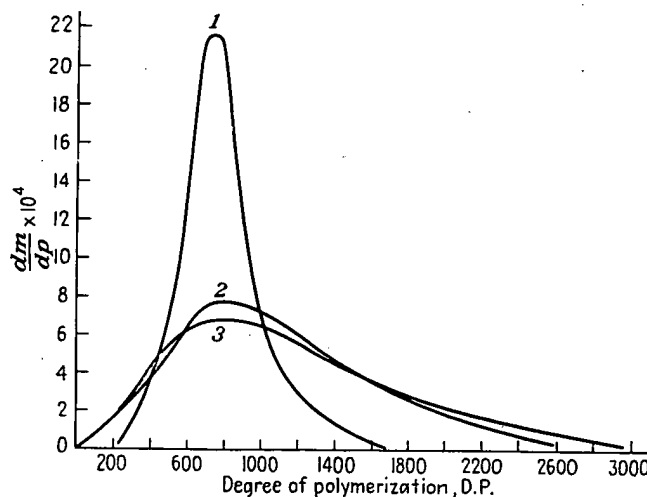


FIG. 1-2. Molecular-weight distribution; dm/dp is change of amount of material with degree of polymerization. Curve 1: cellulose nitrate, average D.P. = 800. Curve 2: polystyrene, average D.P. = 800. Curve 3: theoretical (Eq. 4-9), average D.P. = 800. [G. V. Schulz, *Z. physik. Chem.*, B 32, 27 (1936); B 43, 47 (1939).]

Size distribution may have significant effects upon physical and mechanical behavior. It is obvious that two specimens of a high-polymer material may have the same average molecular weight and yet differ considerably. One may consist of molecules of intermediate sizes with a narrow size distribution, the other of a mixture of very small and very large molecules.

Molecular weights are evaluated by measuring various properties. Colligative properties such as osmotic pressure and freezing-point depression are determined only by the total *number* of molecules; *i.e.*, each molecule affects the measured property to the same extent, regardless of its size, shape, or flexibility. Other properties such as viscosity, scattering of light, and rate of diffusion are influenced not only by the number of molecules but also by their size, shape, and flexibility.

When the molecular weight of a substance composed of simple molecules of identical size is measured via a property from each of these two

broad classes, the molecular-weight values can be identical since the factors of size, etc., are reduced to a constant. On the other hand, when applied to a typical high polymer in which there is a wide range of sizes, the molecular-weight values may be widely divergent. As a consequence, it has been found necessary in this field to establish several molecular-weight definitions, for example, the *number-average molecular weight* \bar{M}_n and the *weight-average molecular weight* \bar{M}_w .

$$\bar{M}_n = \frac{m}{n} = \frac{n_1 M_1 + n_2 M_2 + \dots}{n_1 + n_2 + \dots} = \sum \frac{n_i M_i}{n_i} = \sum N_i M_i \quad (1-6)$$

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \dots}{m_1 + m_2 + \dots} = w_1 M_1 + w_2 M_2 + \dots = \sum w_i M_i \quad (1-7)$$

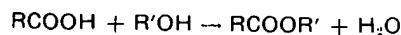
In the above relations, m is the total mass, n is the total number of moles of molecules of all sizes, and N_i and w_i are the mole and weight fractions, respectively, of that particular size of molecule whose molecular weight is M_i .

\bar{M}_n is the molecular weight in the usual classical sense. For a homogeneous material in which all the molecules are of one size, $\bar{M}_w = \bar{M}_n$ and $\bar{M}_w/\bar{M}_n = 1$. When, however, there is a size distribution, \bar{M}_w is greater than \bar{M}_n and the above ratio increases as size disparities grow broader. It is important to bear in mind that a number average imparts relatively greater significance to small molecules while a weight average emphasizes the effect and relative importance of large molecules.

This subject is dealt with at much greater length in Chap. 6, *e.g.*, in Sec. 617.

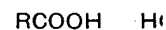
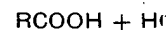
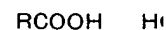
109. Functionality and Polymerization. When may polymerization occur? So far as any particular chemical reaction is concerned, a functional group is merely one which participates *in that reaction*. Functionality may be defined as the ability to form primary valence bonds. As will now be demonstrated, the number and kinds of functional groups present in any chosen set of reactants bear a simple and fundamental relationship to the types of product obtainable from the reaction, and if polymerization is to take place certain functionality requirements must be met. The esterification reaction will be used for illustrative purposes.

110. Mono-monofunctional Systems. The term *mono-monofunctional system* as here used implies a reaction between two molecular species, each possessing but one functional group. In an esterification, this would mean a monocarboxylic acid and a monohydric alcohol. Representing the nonfunctional (so far as esterification is concerned) parts of the reactants as R and R',



In this mono-monofunctional formation of the simple ester incapable of further reaction polymerization does not result from

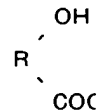
111. Mono-trifunctional Systems. If a monofunctional with a trihydric alcohol, one may consider the reaction



The most extensive molecule of the monomeric triester.

Examination of a large number of functional groups and either polymerization does not occur

112. Bifunctional Systems. If a bifunctional system implies, there is a single molecule of the prop the esterification reaction is of a hydroxycarboxylic acid. The possibilities present themselves react *intramolecularly*, in which



Second, the reaction might occur if the original molecules interact, then hence immediately capable of polymerization is a distinct possibility. The reason why the above process with very long molecules results in a polymer is that it can be either of two types; it can be the interaction of the functional groups at the ends, or the functional groups can interact with one another, leading to a compound.



aps that remain after poly-
s, the important point being
erent from the intermediate
Table 6-1. Carothers' work

MOLECULAR-WEIGHT DETERMINATION

Methods
Acid determination
Salt formation and subsequent determination of metal content
Primary amino group determina- tion
Acid take-up during acetylation
Copper number
Oxidation to carboxyl and sub- sequent acid determination
Reaction with mercaptan and subsequent sulfur determination
Methylation, hydrolysis, and isola- tion of tetramethyl glucose

Acetate determination

Ethoxy determination

Infrared spectrum

ized in Table 1-3, p. 13, is an
successful or applicable for the
always detectable, (2) purifica-
(3) branching may result in
terminations are often, but not
differentiated from the more
physical methods.

t determinations can be made
e methods, which are described
the least of which is the rela-
property being measured and the
tions from which the molecular
olified versions of much more
are not known or cannot be

used for lack of complete data or information. In still other instances, they are entirely empirical. All the equations have the common property of being more applicable in dilute solutions. Frequently an equation holds only in solutions so dilute that accurate measurement becomes impossible. Therefore, in careful work the molecular weight is determined at several concentrations and the correct value obtained by extrapolating to infinite dilution.

The agreement that may be expected from various methods is indicated in Table 6-2.

TABLE 6-2. MOLECULAR WEIGHT OF A FRACTIONATED ω -HYDROXYDECAHOIC ACID POLYMER*

Method	M.W.
End-group titration	25,200
Sedimentation equilibrium	27,000
Diffusion coefficient alone, assuming spherical molecules	2,400,000
Sedimentation velocity alone, assuming spherical molecules	7,600
Diffusion plus sedimentation velocity†	52,000
Viscosity, assuming Staudinger's equation	31,000

* KRAEMER, E. O., and W. D. LANSING, *J. Am. Chem. Soc.*, **55**, 4319 (1933).

† High value probably because frictional coefficient was not the same for sedimentation and diffusion at the concentrations used.

Most of the physical methods may be divided into equilibrium and kinetic methods. Since the former, such as osmotic-pressure determination, are based upon the properties of the system at equilibrium, the equations can theoretically be derived from thermodynamics although mathematical complexities often force the use of simplified relations applicable at infinite dilution. The molecular weight as determined by an equilibrium method is independent of the shape or flexibility of the molecule.

Kinetic methods, such as viscosity determination, are based upon the properties of the system while the molecules are in motion. As a consequence, the derivations of the equations are on a less certain foundation. Usually, calibration of the method and evaluation of the constants depends upon comparison with an equilibrium method. Furthermore, the shape and flexibility of the molecules often have an important influence on the result.

617. Definitions of Molecular Weight. The concept of molecular weight presents little difficulty so long as low-molecular-weight pure substances are dealt with. But, in solution, complications may arise even with low-molecular-weight solutes. For example, consider benzoic acid dissolved in benzene. In concentrated solutions, it associates into double molecules via hydrogen bonding at the carboxyl group [structure (2-C), page 35]. As the solution is diluted, the double molecules dissociate, the dissociation becoming complete at infinite dilution.

Benzoic acid does not undergo similar association in water, where the hydrogen bonding takes place instead between the carboxyl groups and water molecules. An analogous state of affairs often exists in high-polymer solutions, and one would expect a polar solute, such as cellulose acetate, to exhibit considerably greater association in a solvent of low polarity than in one of high polarity. In order to eliminate this effect it is advisable to perform measurements in at least two solvents of differing polarity, to carry out the measurements at as low concentrations as possible, and to extrapolate the results to infinite dilution. In some cases, it is further advisable to make measurements at two different temperatures because increase in temperature decreases association.

The greatest complication in measurements on high polymers is the presence of molecules of different sizes, as a consequence of which an average molecular weight is obtained. Each method of investigation yields a particular type of average. With a single molecular-weight species all these "averages" assume the same value; but, the greater the polymolecularity, the greater the disparity among them.

The two most important types of average molecular weights, the number average and weight average, have already been defined (Sec. 108). These will nevertheless be reviewed here and compared with two additional types of averages.

Number-average molecular weight is the ordinary average molecular weight usually meant and is defined by

$$\bar{M}_n = \frac{\text{total mass}}{\text{total no. of moles}} = \frac{m}{n}$$

It is the average given by methods that count molecules, such as end-group analysis and osmotic methods.

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots}{n_1 + n_2 + \dots} = \frac{\sum n_i M_i}{\sum n_i} = \sum N_i M_i$$

Weight-average molecular weight is given by methods that depend on the weights of molecules present, such as light scattering and sedimentation equilibrium under certain conditions of measurement.

$$\bar{M}_w = \frac{m_1 M_1 + m_2 M_2 + \dots}{m_1 + m_2 + \dots} = \sum w_i M_i = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

The z-average molecular weight is obtained by sedimentation equilibrium under other conditions of measurement and is defined by

$$\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}$$

Viscosity-average measurements,

$$\bar{M}_v = \left(\frac{m_1 M_1^a + m_2 M_2^a}{m_1 + m_2} \right)^{1/a}$$

where a is a constant (6-50)]. When a equals 1, \bar{M}_v is the weight average.

Table 6-3 compares the various averages calculated for mixtures of two species.

TABLE 6-3 Comparison of various averages (Calculated for hypothetical mixture of two species)

Species	Number average, \bar{M}_n	Weight average, \bar{M}_w	Viscosity average, \bar{M}_v	z average, \bar{M}_z
1	100	100	100	100
2	100	100	100	100
Total	200	200	200	200
Number average, \bar{M}_n	100			
Viscosity average, \bar{M}_v		100		
Weight average, \bar{M}_w			100	
Viscosity average, \bar{M}_v				100
z average, \bar{M}_z				100

Since various methods are used to determine molecular weight, it is essential to know the basis of each method. Since this is a very precise and delicate process, it has its own pitfalls, as do all measurements. Errors may arise from the use of different methods or from effects of shape and flexibility.

618. Osmotic Measurement. Lowering of boiling point, depression of solution are all interrelated phenomena. Historically, the osmotic-pressure law has been collectively, osmotic properties.

KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

THIRD EDITION

VOLUME 20

REFRACTORIES
TO
SILK



A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

1982

Table 6. Properties of Siloxane Oligomers^a

Compound	CAS Registry No.	Boiling point, °C _{kPa} ^b	Density <i>d</i> ²⁰ , g/cm ³	Refractive index, <i>n</i> _D ²⁰	Melting point, °C
[(C ₆ H ₅) ₂ SiO] ₄	[546-56-5]	335 _{0.13}			200
[(CH ₃)(C ₆ H ₅)SiO] ₄	[77-63-4]	237 _{0.13-0.67}	1.183	1.5461	99
(CH ₃) ₃ SiOSi(C ₆ H ₅) ₂ OSi(CH ₃) ₃	[797-77-3]	172 _{2.4}	0.984	1.4927	
[(CF ₃ CH ₂ CH ₂)(CH ₃)SiO] ₄	[429-67-4]	134 _{0.4}	1.255	1.3724	
[(CH ₂ =CH)(CH ₃)SiO] ₄	[2554-06-5]	111 _{1.3}	0.9875	1.4342	-43.5
(CH ₃) ₃ Si[OSiH(CH ₃) ₂ OSi(CH ₃) ₃]	[16066-09-4]	177	0.8559	1.3854	
[(CH ₃)(H)SiO] ₄	[2370-88-9]	134	0.9912	1.3870	-69

^a Refs. 16 and 88.^b To convert kPa to mm Hg, multiply by 7.5.

Silicone Fluids

Dimethylsilicone fluids are made by catalyzed equilibration of dimethyl silicone stock, ie, the crude fluid or distilled cyclic polymers, with a source of the chain terminator, (CH₃)₃SiO_{0.5}. As described above, this reaction produces mixtures of MD_nM and D_m polymers. The ratio of M to D in the charge controls the average molecular weight and the viscosity of the product. For example, a 50 mm²/s (= cSt) fluid has an average molecular weight of ca 3000, a 350-mm²/s fluid ca 15,000, and a 1,000-mm²/s fluid ca 25,000. For relatively low viscosity fluids, the process can be run at ca 180°C in glass-lined reactors with acid clay catalysts or at lower temperatures with sulfuric acid. Both batch and continuous processing are used (28).

Alkaline catalysts are used for the production of high viscosity fluids or gums. These polymers can be processed batchwise in kettles or continuously in a heated tube with stirring (89). Polymerization is continued in the case of gums to make polymers of >500,000 av mol wt and 10⁷ mm²/s (= cSt) viscosity. Some gums contain vinyl or phenyl substituents, which are introduced by copolymerizing (CH₃)₂SiO with vinyl or phenylsiloxanes. Phenyl substituents are added as [(C₆H₅)₂SiO]_n or [(CH₃)-(C₆H₅)SiO]_n. Vinyl substituents are added as [(CH₃)(CH₂=CH)SiO]_n or [(CH₃)₂(CH₂=CH)SiO]_{0.5}, or both.

In most instances, the fluid equilibrate is devolatilized by heat and vacuum after catalyst deactivation. Both equilibration and devolatilization can be carried out in batch or continuous process systems. Fluids are sometimes blended in order to make fluids of intermediate viscosities. Since the properties of a polymer depend upon molecular weight distribution as well as upon average molecular weight, blending can affect physical properties appreciably. Blends of fluids of widely different viscosities are less Newtonian in behavior than those with normal molecular weight distribution. Some properties of commercial silicone fluids are given in Table 7, and silicone-fluid viscosity is shown as a function of temperature in Figure 1. These viscosity-temperature profiles fit the following general equation:

$$\log (\eta + B) = A \log T + C$$

where *A*, *B*, and *C* are constants (92). Data for two nonsilicone fluids are plotted in Figure 1 to illustrate the steeper slopes characteristic of such materials. Silicones with phenyl, trifluoropropyl, or large alkyl substituents also show steeper slopes when plotted in this way.

81. K. E. Polmanteer and M. J. Hunter, *J. Appl. Polym. Sci.* 1, 3 (1959).
82. T. V. Koroleva, T. A. Krasovskaya, M. V. Sobolevskii, L. V. Gornets, and Yu. E. Raskin, *Soviet Plastics*, 28 (Jan. 1967).
83. K. B. Yerrick and H. N. Beck, *Rubber Chem. Technol.* 37, 261 (1964).
84. H. M. Schiefer and J. VanDyke, *Am. Soc. Lubric. Eng. Trans.* 7, 32 (1964).
85. H. M. Schiefer, *Am. Soc. Lubric. Eng. Trans.* 9, 36 (1966).
86. U.S. Pat. 2,834,748 (May 13, 1958), D. L. Bailey and F. M. O'Connor (to Union Carbide Company).
87. R. N. Meals, *Ann. N.Y. Acad. Sci.* 125, 137 (1964).
88. *Gmelins Handbuch der anorganischen Chemie*, 8th ed., System Number 15, Silicium, Teil C, Organische Siliciumverbindungen, Verlag Chemie G.m.b.H., Weinheim, FRG, 1958.
89. N. Kirk, *Ind. Eng. Chem.* 51, 515 (1959).
90. *Silicone Fluids*, F-46182, Union Carbide Corporation, New York, 1978.
91. *Silicone Fluids*, S-9E, General Electric Company, Waterford, N.Y., 1980.
92. *Physical Properties of Lubricants*, American Society for Testing Materials, Philadelphia, Pa., 1949.
93. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* 77, 129 (1949).
94. *Ibid.*, p. 115.
95. W. Noll, *Kolloid-Z* 211, 98 (1966).
96. H. W. Fox, P. W. Taylor, and W. A. Zisman, *Ind. Eng. Chem.* 39, 1401 (1947).
97. A. A. Bondi, *Physical Chemistry of Lubricating Oils*, Reinhold Publishing Company, New York, 1951.
98. A. Weissler, *J. Am. Chem. Soc.* 71, 93 (1949).
99. E. B. Baker, A. J. Barry, and M. J. Hunter, *Ind. Eng. Chem.* 38, 1117 (1946).
100. F. Clark, *Insulating Materials for Design and Engineering Practice*, John Wiley & Sons, Inc., New York, 1962.
101. P. Cannon, L. E. St. Pierre, and A. A. Miller, *J. Chem. Eng. Data* 5, 236 (1960).
102. G. E. Vogel and F. O. Stark, *J. Chem. Eng. Data* 9, 599 (1964).
103. Unpublished data based on measurements using ^{14}C labeled dimethylpolysiloxane, General Electric Company, Waterford, N.Y., May 16, 1958.
104. *Silicone Fluids in Radiation Environment*, CDS-4176, General Electric Company, Waterford, N.Y., 1975.
105. D. Tabor and W. D. Winer, *Am. Soc. Lubric. Eng. Trans.* 8, 69 (1965).
106. H. R. Baker, R. E. Kagarise, J. G. O'Rear, and P. J. Sniegoski, *J. Chem. Eng. Data* 11, 110 (1966).
107. U.S. Pat. 3,865,784 (Feb. 11, 1975), R. S. Neale and A. N. Pines (to Union Carbide Corporation).
108. M. V. Sobolevskii and co-workers, *Plast. Massy* 3, 13 (1962).
109. I. Lipovetz and A. Borbely, *Period. Polytech. Chem. Eng.* 2, 259 (1958).
110. A. Charlesby, *Proc. Roy. Soc. A* 230, 120 (1955).
111. A. M. Wrobel, M. R. Wertheimer, J. Deb, and H. P. Schreiber, *J. Macromolecular Sci.* A14, 321 (1980).
112. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1962.
113. R. K. Jenkins, *J. Polymer Sci.* A1(4), 2161 (1966).
114. U.S. Pat. 3,812,081 (May 21, 1974), W. E. Dennes and G. E. Vogel (to Dow Corning Corporation).
115. H. C. Smith, D. L. Sweeney, and E. G. Bittner, *Insulation (Libertyville)* 13(7), 257, 268 (1967).
116. F. J. Modic, *Adhes. Age* 5 (Dec. 1962).
117. U.S. Pat. 3,986,997 (Oct. 19, 1976), H. A. Clark (to Dow Corning Corporation).
118. U.S. Pat. 4,246,038 (Jan. 20, 1981), H. A. Vaughn and F. F. Holub (to General Electric Company).
119. U.S. Pat. 2,449,572 (Sept. 21, 1948), C. E. Welsh (to General Electric Company).
120. Brit. Pat. 841,825 (July 20, 1960), (to Wacker-Chemie G.m.b.H.).
121. U.S. 3,205,283 (Sept. 7, 1965), F. J. Modic (to General Electric Company).
122. U.S. Pat. 3,801,544 (April 2, 1974), A. E. Mink and D. D. Mitchell (to Dow Corning Corporation).
123. U.S. Pat. 4,223,072 (Sept. 16, 1980), R. H. Bakey and L. A. Harris (to Dow Corning Corporation).
124. U.S. Pat. 4,243,721 (Jan. 6, 1981), R. H. Bakey and L. A. Harris (to Dow Corning Corporation).
125. S. Fordham, *Silicones*, Philosophical Library, New York, 1960.
126. M. D. Beers in I. Skeist, ed., *Handbook of Adhesives*, D. Van Nostrand Company, New York, 1977.
127. A. M. Bueche, *J. Poly. Sci.* 25, 139 (1957).
128. B. B. Boonstra, H. Cochrane, and E. M. Dannenberg, *Rubber Chem. Technol.* 48, 448 (1975).

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY

VOL. LXXVII

APRIL-JUNE

1955

W. ALBERT NOYES, JR., EDITOR

ALLEN D. BLISS

ASSISTANT EDITORS

MARSHALL GATES

EDITORIAL BOARD

JOHN C. BAILAR, JR.
PAUL D. BARTLETT
HERBERT E. CARTER
ARTHUR C. COPE
PAUL C. CROSS
ARTHUR W. DAVIDSON
WILLIAM VON E. DOERING
JOHN T. EDSALL

PAUL J. FLORY
HAROLD S. JOHNSTON
I. M. KOLTHOFF
WALTER M. LAUER
JOHN A. LEERMAKERS
JAMES J. LINGANE
FRANK R. MAYO
S. M. McELVAIN

MELVIN S. NEWMAN
FREDERICK D. ROSSINI
VERNER SCHOMAKER
GLENN T. SEABORG
ESMOND E. SNELL
WILLIAM E. VAUGHAN
W. H. WOODSTOCK
L. ZECHMEISTER

EASTON, PA.
MACE PRINTING COMPANY
1955

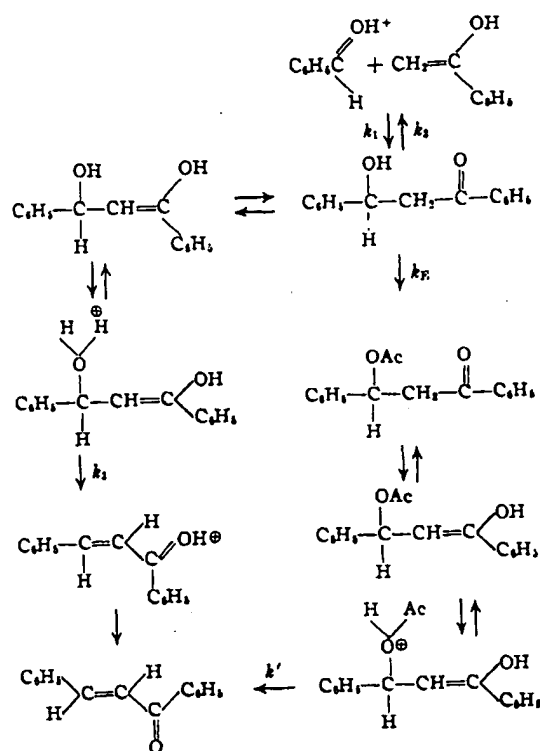
compared with an extrapolated value from the data reported earlier¹ of -4.97.

More extensive data determined in anhydrous acetic acid are presented in Table V. At higher concentrations of acetophenone the value of the pseudo unimolecular rate constant k_{im} does not increase as rapidly as would be predicted, as shown in Fig. 2. At the higher concentrations of acetophenone, the rate of the condensation approaches the rate of the elimination, k_2' .

Conclusions Regarding the Mechanism of the Forward Condensation Reaction.—Because of the complexity of the steps succeeding the actual bond-forming reaction, where even the observed rate of appearance of chalcone from the ketol in acid is a function of several competing reactions, it is not feasible to determine all of the rate constants from the present data.

However it may be concluded that the rate of the dehydration of the ketol is faster than the rate of the loss of acetic acid from the ketol acetate. This result is probably due to the greater basicity of the alcohol as compared to the ester.

One may present a fairly detailed picture of the pathway(s) by which chalcone arises under the conditions investigated. Such a reaction scheme is outlined below. Under the differing experimental conditions investigated, the value of the bimolecular rate constant determined is not exactly the same in both the anhydrous and the wet acetic acid media, at the same H_0 . This difference is presumably due to the difference in the branching ratio of the different possible reactions of the intermediate ketol. It is also attractive to suggest that the elimination step takes place through the intermediate



enol. The rate of enolization is of the appropriate order of magnitude for this to be feasible.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Kinetics of the Polymerization of a Cyclic Dimethylsiloxane¹

BY W. T. GRUBB AND ROBERT C. OSTHOFF

RECEIVED OCTOBER 13, 1954

Cyclic dimethylsiloxanes are converted into high polymers by the action of potassium hydroxide at elevated temperatures. The kinetics of this process has been studied using the monomer, octamethylcyclotetrasiloxane (I). Precipitation and distillation analysis of this system at small conversions reveals that I and high polymer make up at least 90% of the material present. Because of this, the well known theories of polymer-solvent systems have been applied. In particular, the vapor pressure above the polymerizing system is a convenient measure of the extent of reaction. The kinetics have been measured by continuously monitoring the vapor pressure above the polymerizing solution. The reaction proceeds at a rate which is first order in the volume fraction of I in the solution attaining an equilibrium at about 94% polymer. A reversion reaction of the polymer takes place at a rate proportional to the volume fraction of polymer present. The rate law based on these concepts is in excellent agreement with the experimental kinetics. The apparent activation energy of the over-all polymerization is found to be 19.6 kcal. The rate of the polymerization is proportional to the square root of the potassium hydroxide concentration.

Many cyclic siloxanes undergo reaction in the presence of acidic or basic catalysts to form high molecular weight siloxane polymers. For example, dimethylsiloxane polymers may be formed from low molecular weight octamethylcyclotetrasiloxane (I) by the action of potassium hydroxide or other alkali metal hydroxides at elevated temperatures.¹ Some qualitative features of this reaction

have been investigated previously,² and a mechanism involving the formation of intermediate alkali metal silanates was proposed, but no exact kinetic data were obtained. It was therefore the purpose of the present investigation to develop a suitable experimental method for measuring the kinetics of polymerization of I under carefully controlled conditions and to investigate the effects of temperature and other conditions upon the reaction

(1) Presented at the 126th meeting of the American Chemical Society, New York, N. Y., September, 1954.

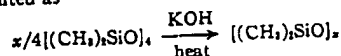
(2) J. F. Hyde, U. S. Patent 2,490,357 (December 8, 1949).

(3) D. T. Hurd, R. C. Osthoff and M. L. Corrin, THIS JOURNAL, 76, 249 (1954).

rate in order to obtain a better understanding of the mechanism and thermodynamics of the reaction.

Experimental

General Considerations.—The polymerization of I may be represented as



The cyclic structure I rearranges to form a long chain molecule which is terminated by small traces of various end-groups. These include silanols formed from the reaction of water with the siloxane, silanols formed from the reaction of potassium hydroxide with the siloxane, and the monofunctional siloxane end group $(\text{CH}_3)_2\text{SiO}_2\text{H}$ which may be accidentally present. The rearrangement reaction of I containing large amounts of monofunctional siloxanes in the presence of basic catalysts has been studied previously by viscosity measurements.⁴ In order to study the formation of high molecular weight polymers by the above reaction, it was necessary to maintain conditions of high purity at all times during the reaction. A suitable method for measuring the polymerization rates would consist of some physical measurement not involving sampling or exposure of the system to atmospheric contamination (moisture, etc.).

The most successful method was found to be the continuous monitoring of the vapor pressure above the polymerizing system. In order to interpret such measurements, the composition of the system after short polymerization times was analyzed by three methods to be described. The results of these analyses permitted an unambiguous interpretation of the vapor pressure measurements in terms of the amount of I reacted to form non-volatile products.

Preparation of Materials. A. Tetramer (Octamethylcyclotetrasiloxane).—Crude I was obtained by distilling the products of hydrolysis of dimethyldichlorosilane.⁵ This material was then dried over calcium hydride and redistilled to obtain tetramer of 99.8 mole % purity, b.p. 175°, n_D^{20} 1.3968.⁶ The mean water content of this material was found by Karl Fischer titration⁷ to be 30 ± 10 parts per million.

B. Potassium Hydroxide Catalyst.—Potassium hydroxide is not sufficiently soluble in I at room temperature to permit the use of homogeneous solutions to catalyze the polymerization reaction. It has been necessary, therefore, to prepare suspensions of finely divided potassium hydroxide in I in the concentration range of 0.01% by weight of base. Preliminary investigations showed that suspensions in the desired 0.01% concentration range are not stable for periods of a few days, are difficult to analyze accurately, and are somewhat sensitive to prior treatment of the glassware in which they are prepared. In order to avoid these difficulties, a concentrated suspension (ca. 0.2% by weight) was first prepared and standardized in the following manner.

Pellets of potassium hydroxide (reagent grade containing about 85% potassium hydroxide and 15% water) were ground as fine as possible in a nitrogen dry-box (dew point of the nitrogen was less than -50°). Approximately two grams of this powder was then agitated with 250 ml. of I in a Waring Blendor for five minutes under a blanket of dry nitrogen. The suspension obtained in this fashion was then poured into a storage flask and allowed to stand overnight. It was then transferred into a second storage flask, leaving behind any large particles of potassium hydroxide and/or materials adhering to the flask walls.

The analysis of the suspension was then carried out by pipetting a sample of suitable size, shaking it thoroughly with twice its volume of distilled water, and then titrating the two-phase system against standard 0.1 N aqueous hydrogen chloride solution using two indicators (phenolphthalein and methyl orange). The correction for the presence of potassium carbonate was made in the usual manner and usually amounted to about 5% of the potassium hydroxide. Satisfactory homogeneity of the suspension during sampling has been achieved by means of continuous magnetic stirring

during sampling. Reproducible extraction of the potassium hydroxide into the water layer was achieved only by several minutes of vigorous shaking. When prepared in this manner, the concentrated suspension gave reproducible analyses (within 1%) over periods of one month or more. These suspensions contained 2–4 mg. ml.⁻¹ of potassium hydroxide in I.

In order to prepare a suspension for a polymerization rate experiment, the calculated amount of the concentrated suspension was diluted to form 250 ml. of suspension of the desired concentration, i.e., 0.01% by weight of potassium hydroxide. The volumetric flasks used in these operations had been steamed previously for two hours and oven dried to remove any acidic surface contaminants present.⁸

For the rate studies, about 35 ml. of the dilute suspension was added by means of a hypodermic syringe to an isoteniscope, or a suitable bulb, the construction and operation of both of which are described below. The authors estimate that the procedure just described results in the formation of a suspension of potassium hydroxide of concentration 0.01% which is known with a relative error of $\pm 2\%$.

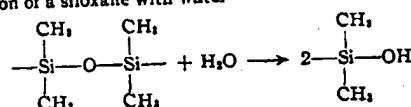
An analysis by Karl Fischer titration⁹ was carried out upon two 250-ml. batches of I plus 0.01% potassium hydroxide with the results indicated in Table I. It will be noted that water, potassium hydroxide,¹⁰ and silanol¹¹ are all equivalent mole-for-mole toward reaction with the Karl Fischer reagent.

TABLE I
WATER ANALYSES IN TETRAMER-POTASSIUM HYDROXIDE SUSPENSIONS

Batch no.	Total H ₂ O, moles/l.	Initial ^b	KOH, ^c moles l. ⁻¹
1	0.0063	0.0020	0.0014
2	.0060	.0020	.0014

^a Total apparent water, includes the KOH, H₂O and $\geq \text{SiOH}$. ^b Determined by titration of I blank. ^c Calculated based on assumption that the Reagent Grade KOH contained 85% KOH and 15% H₂O.

The difference, $[0.0060 - (0.0020 + 0.0014)] = 0.0026$ moles l.⁻¹ of material titratable as water, may be accounted for either by moisture picked up during handling or by the reaction of a siloxane with water



The authors suggest the latter explanation as causing the increase in apparent water, since methods of handling the I have been tested previously and found to introduce little or no atmospheric moisture.⁷

C. Potassium Silanolate Catalyst.—A modification of the method of Hyde¹¹ was employed for the preparation of the potassium silanolate catalyst. Anhydrous toluene containing about 33% by weight of hexamethylcyclotrisiloxane and about 0.5% by weight of finely powdered reagent grade potassium hydroxide was refluxed under dry nitrogen and the water formed by the reaction of the potassium hydroxide with the siloxane (to form SiOK and SiOH followed by condensation of the silanols) was removed and measured by a Dean-Stark trap. After the theoretical amount of water had been recovered, the solution was refluxed for 10 more hours and no further water was formed. The total reflux time was 24 hours. The toluene solution then consisted of a solution of $\text{KO}[(\text{CH}_3)_2\text{SiO}]_x\text{K}$. This material was analyzed by conventional acid-base titration in a manner similar to that employed for the suspensions of potassium hydroxide in I. In order to prepare a solution for a polymerization experiment, a suitable amount of the toluene solution of the silanolate was introduced into the polymerization bulb and pumped for 24 hours in high vacuum to remove all the toluene leaving behind the oily silanolate. More I was then added and the polymerization experiment carried out in the

(4) S. W. Kantor, W. T. Grubb and R. C. Osthoff, *This Journal*, **76**, 5100 (1954).

(5) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 258 (1946).

(6) R. C. Osthoff and W. T. Grubb, *ibid.*, **76**, 399 (1954).

(7) W. T. Grubb, *ibid.*, **76**, 3408 (1954).

(8) M. L. Corbis, private communication, 1953.

(9) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, New York, N. Y., 1948, p. 259.

(10) H. Gilman and L. S. Miller, *This Journal*, **75**, 2367 (1951).

(11) J. F. Hyde, U. S. Patent 2,667,110 (Sept. 4, 1951).

same manner described for the experiments using potassium hydroxide.

D. Preparation of Solvents for Use.—Baker and Adamson C.P. toluene was dried over calcium hydride and distilled. Baker and Adamson C.P. methanol was used without further treatment.

Determination of the Rate of Disappearance of I by Distillation.—I was polymerized for various times and the unchanged I was recovered by distillation. In these experiments, about 150 ml. of the I-potassium hydroxide suspension of 0.01% base concentration was prepared in the usual fashion (*vide supra*) and placed in a 180-ml. seal-off bulb. The suspension was then thoroughly out-gassed¹³ and the bulb was sealed under high vacuum. These bulbs were then placed in a silicone oil-bath at $140.0 \pm 0.1^\circ$ for various times. The bulbs were removed from the bath at the appropriate times and quenched in an ice-bath and then a liquid nitrogen bath to stop the polymerization reaction. The bulbs were then opened and 0.5 g. of powdered iodine was added to neutralize the potassium hydroxide catalyst.¹³ A known weight of the partially polymerized I was then added to a given amount of decamethyltetrasiloxane MD₂M, ($M = [(CH_3)_2SiO]_n$)—and $D = -[(CH_3)_2SiO]—$. The purification of MD₂M has been described previously¹⁴ and the mixture was set aside until a homogeneous solution was obtained. At this time about 1 g. of powdered silver was added to the solution to react with the excess iodine present. This heterogeneous reaction of iodine and silver required about two weeks at room temperature. After the solutions had become colorless, I was determined by quantitative distillation techniques. The amount of I which had reacted was then evaluated by calculation.

In general, about 140 g. of the partially polymerized I was added to the MD₂M. However, the amount of MD₂M was increased as the polymerization time was lengthened from 7.5 to 90 minutes in order to maintain a sufficiently low viscosity for the distillation sample. For example, the amount of MD₂M employed was increased from 100 to 700 g. as the polymerization time was increased from 7.5 to 90 minutes. The MD₂M functioned not solely as a solvent, but also as a "chaser" for the distillation of I.¹⁴

In order to determine an estimate of the accuracy with which a quantitative distillation of this type could be carried out a solution consisting of 50.0% by weight of I and 50.0% by weight of neutral polydimethylsiloxane was prepared. About 140 g. of the 50-50 solution was added to an approximately equal weight of MD₂M. The solution was treated with iodine and silver powder as described previously. Upon distillation, the I concentration in the original solution was determined to be 50.2% by weight (made up to 50.0%). Thus, the accuracy of this type of determination was considered to be sufficient for the authors' purposes.

This procedure was applied to a series of runs with I containing 0.01% of potassium hydroxide. The bulbs used in these experiments were subjected to mechanical agitation during the entire period of time that they were in the bath, in order to aid in the attainment of thermal equilibrium. The amounts of I which were consumed after various polymerization times, as determined by distillation, are recorded in Table II.

TABLE II
RATE OF DISAPPEARANCE OF OCTAMETHYLCYCLOTETRA-SILOXANE AT 140° WITH 0.01% POTASSIUM HYDROXIDE

Polymerization time (min.)	% Tetramer consumed (wt.)	Polymerization time (min.)	% Tetramer consumed (wt.)
7.5	0	45	56.2
15	11.4	75	84.4
22.5	19.0	90	84.8
30	33.1	1080	94.9
35	41.0		

The equilibrium amount of I is about 5% by weight under the conditions of the experiment.

An examination of the data of Table II indicates that tetramer consumption does not begin until ca. 10 minutes

after immersion in the 140° bath. This was at least in part due to the time delay in reaching temperature. To determine the time-temperature relationship, a single junction copper-constantan thermocouple was placed in the center of a polymerization bulb containing 150 ml. of I at 25° . The thermocouple leads were attached to a Leeds and Northrup recording potentiometer, and the bulb was immersed in the bath. The center of the bulb reached 132° after 10 minutes, and the final temperature of 140° was obtained after a total time of 20-25 minutes in the bath. Thus, some of the reaction occurred at the lower temperatures present during the early stages.

The Determination of the Rate of Polymer Formation by Precipitation Experiments.—Another approach to the kinetic study of the polymerization of I was the precipitation of the polymer after various polymerization times and the determination of the amount of high molecular weight material. In carrying out such a study, the same general procedure was used as in the case of the distillation experiments described above. However, when the partially polymerized I from the 140° bath had been quenched and treated with iodine, the material was dissolved in anhydrous toluene rather than in MD₂M. The amount of toluene was increased with increasing polymerization times in order that the final solution would contain between 10 and 20% by weight of polymeric material. Once a homogeneous solution was obtained, about one gram of powdered silver was added to destroy the excess iodine. The solution was then suction filtered with ca. 5% of Johns-Manville Co. Celite 270. The polymer was obtained by precipitation with a large excess of C.P. methanol. After the polymer had settled, it was washed five times with methanol and placed in a vacuum desiccator. The polymer was then pumped until the pressure over the gum was reduced to less than 60μ Hg and to constant weight. At this point, the amount of gum was determined.

A check determination was carried out upon a solution consisting of a synthetic mixture of 50.0% by weight of washed gum and 50.0% by weight of I. When the procedure outlined above was followed, precipitation led to a value of 50.2% of polymer in excellent agreement with the original composition.

A large series of runs of various times of polymerization were carried out and the amount of polymer determined. These data are summarized in Table III in which the polymerization time and the percentage of polymer are presented.

TABLE III
RATE OF FORMATION OF POLYMER AS A FUNCTION OF POLYMERIZATION TIME WITH 0.01% POTASSIUM HYDROXIDE AT 140°

Polymerization time (min.)	% Polymer	Polymerization time (min.)	% Polymer
7.5	0	45	42.2
15	ca. 1	60	63.2
22.5	10.3	60	62.2
22.5	13.3	90	74.5
30	23.0	90	79.4
30	24.0	90	76.8
45	43.2	1380	84.6
45	45.5		

It will be seen that the same general type of curve was obtained as in the case of the distillation experiments, including the time delay. However, the precipitated polymer is generally somewhat less than the amount of I which has been consumed. This is indicative of incomplete precipitation which may be due to the presence of intermediate molecular weight fractions. Other independent experiments have shown that all molecular weights down to ca. 10,000 are precipitated under the conditions of these experiments (this molecular weight corresponds to about 14 $[(CH_3)_2SiO]$ units).

Determination of the Rate of Polymer Formation by Vacuum Devolatilization.—An alternate method for the determination of the amount of polymer formed was investigated. This consisted of treating a portion of the partially polymerized I with powdered iodine to destroy the potassium hydroxide. At this point, a small (about 1 g.)

(12) W. T. Grubb and R. C. Ostboff, *This Journal*, **78**, 2230 (1953).

(13) R. C. Ostboff, A. M. Bueche and W. T. Grubb, *ibid.*, **76**, 4659 (1954).

(14) B. M. Hadsell, private communication, 1954.

sample of the gum was placed in a high vacuum system and pumped to constant weight (± 5 mg.). The results of several experiments of this type are summarized in Table IV.

TABLE IV

AMOUNT OF POLYMER FORMED AT VARIOUS POLYMERIZATION TIMES WITH 0.01 % POTASSIUM HYDROXIDE CATALYST AT 140° (PUMPING RUNS)

Polymerization time (min.)	% Polymer	Polymerization time (min.)	% Polymer
22.5	17.5	70	67.8
30	27.4	80	70.2
45	41.7	90	81.3
45	46.6	1080	87.8
60	61.3		

It is apparent that pumping and precipitation methods give comparable results. However, the distillation experiments indicate that an intermediate molecular weight fraction is formed during the course of the polymerization reaction, as mentioned previously. This fraction must have a much lower vapor pressure than I itself and may well consist of growing polymer chains. The probability of forming cycles in this molecular weight range is low.¹¹

Molecular Weight Determinations.—It was of interest to determine the molecular weights of the polymers obtained from the 140° polymerization of tetramer with 0.01% of potassium hydroxide at various extents of polymerization. For this purpose, the decatalyzed samples from the precipitation experiments were employed.

The molecular weights were determined from the intrinsic viscosity in toluene solutions using Barry's equation¹²

$$[\eta] = 2 \times 10^{-4} M_n^{0.66} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and M_n is the number average molecular weight. In Table V the number average molecular weights of various samples are tabulated against polymerization time and percentage conversion to polymer.

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHT VS. PER CENT. CONVERSION TO POLYMER AND POLYMERIZATION TIME

$M_n \times 10^{-4}$	Polymerization time (min.)	% Conversion ^a	$M_n \times 10^{-4}$	Polymerization time (min.)	% Conversion ^a
1.86	22.5	11.8	8.75	80	62.7
1.75	22.5	11.8	9.20	60	62.7
3.07	30	23.5	10.06	60	62.7
4.33	30	23.5	8.90	70	65 ^b
7.59	45	43.6	8.84	90	76.9
5.78	45	43.6			

^a Mean data of Table IV. ^b Estimated from Table IV.

An examination of Table V indicates that the molecular weight extrapolates to approximately zero at zero per cent. conversion. Also, the molecular weight is roughly proportional to the per cent. conversion to polymer up to about 60%. It is important to the interpretation of the vapor pressure experiments that the polymer molecular weight is high ($>10^4$) after only 10% conversion.

The Determination of Rates of Polymerization by Vapor Pressure Measurements.—The preceding results have shown that the polymerization of I takes place by the continuous utilization of monomer units and its conversion into relatively high molecular weight polydimethylsiloxane chains. It has been established that these chains have a number average molecular weight of ca. 100,000 (330 units of I) after approximately 10% conversion, and that I is the major volatile component in the polymerizing system. Thus, the polymerizing system should obey the thermodynamic equations for solvent-polymer solutions. For instance, Huggins^{17,18} has shown that

$$\Delta F_0 = RT \left\{ \ln \phi_0 + \left[1 - \frac{1}{m} \right] \phi_p + \mu \phi_p^2 \right\} \quad (2)$$

where ΔF_0 is the partial molal free energy of the solvent, ϕ_0 is the volume fraction of the solvent, ϕ_p is the volume fraction of the polymer, R is the gas constant, T is the absolute temperature, m is the number of elementary units in the polymer, and μ is the polymer-solvent interaction parameter.

If ΔF_0 is replaced by $RT \ln P/P_0$ where P is the vapor pressure of the solvent in the solution and P_0 is the vapor pressure of pure solvent at the same temperature, it is evident that by measurements of vapor pressure above a solvent-polymer mixture, one might directly determine ϕ_0 , provided the empirical constant μ has been obtained for the system in question. Application of such a method to the polymerization of I is simplified by neglecting the term $1/m$ which becomes negligible above 10% conversion, since m is very large. The constant μ for this system has been previously evaluated by measurements of vapor pressure¹ and has a mean value of 0.28 for the system I polydimethylsiloxane at 140°. However, in this type of system, considerable variation in the value of μ occurs over the range of ϕ_0 from zero to one.^{19,20} The experimental ϕ_0 vs. P/P_0 points has been used to calculate a table of values of ϕ_0 and $(1 - \phi_0)$ as a function of the relative pressure, P/P_0 , see Table VI. The individual values have been interpolated from previous results.¹ Although the values of Table VI have been obtained from experimental data at one temperature, 140.0°, they may be applied over a considerable range of temperatures in the vicinity of 140° because the heat of mixing of polymer and I has been shown to be zero.⁴

TABLE VI

RELATIVE PRESSURES (P/P_0) VS. VOLUME FRACTION (ϕ_0) OF I IN POLYMER SOLUTION

(P/P_0)	ϕ_0	$(1 - \phi_0)$	(P/P_0)	ϕ_0	$(1 - \phi_0)$
0.20	0.060	0.940	0.70	0.300	0.700
2	.068	.932	1	.306	.694
4	.075	.925	2	.313	.687
6	.082	.918	3	.320	.680
8	.090	.910	4	.327	.673
0.30	0.096	0.904	5	.335	.665
2	.103	.897	6	.342	.658
4	.111	.889	7	.349	.651
6	.118	.882	8	.356	.644
8	.130	.870	9	.365	.635
0.40	0.140	0.860	0.80	0.373	0.627
2	.150	.850	1	.382	.618
4	.160	.840	2	.391	.609
6	.170	.830	3	.401	.599
8	.180	.820	4	.411	.589
0.50	0.191	0.809	5	.421	.579
2	.200	.800	6	.432	.568
4	.212	.788	7	.445	.555
6	.224	.776	8	.459	.542
8	.234	.766	9	.473	.527
0.60	0.245	0.755	0.90	0.488	0.512
1	.250	.750	1	.507	.493
2	.255	.745	2	.527	.473
3	.260	.740	3	.546	.454
4	.265	.735	4	.572	.428
5	.270	.730	5	.600	.400
6	.275	.725	6	.633	.367
7	.281	.719	7	.675	.325
8	.287	.713	8	.730	.270
9	.293	.707	9	.805	.195
0.70	0.300	0.700	0.995	.850	.150
			0.997	.875	.125

The method of measuring the vapor pressures has been described previously.⁴ The modified isoteniscope of Smith

(15) D. W. Scott, *This Journal*, **68**, 2294 (1946).

(16) A. J. Barry, *J. App. Phys.*, **17**, 1020 (1946).

(17) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).

(18) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **48**, 1 (1942).

(19) G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, **38**, 147 (1942).

(20) G. Gee and W. J. C. Orr, *ibid.*, **42**, 507 (1946).

and Menzies^{21,22} was further modified by the use of a larger bulb to accommodate the vapor pressure sample (ca. 70 ml. total volume). An approximately 35-ml. sample of I plus 0.01% potassium hydroxide was introduced through a constricted side arm into the bulb using a hypodermic syringe. After the isoteniscope was sealed at the constriction, the sample was thoroughly out-gassed and the mercury was then tipped into the "U" section to form a differential manometer. The vapor pressures were then measured in the conventional fashion. The bulb and differential manometer sections of the isoteniscope were maintained at temperature by immersing them in a silicone oil thermostat ($\pm 0.1^\circ$).

A typical experiment will be described in detail. Figure 1 presents a plot of P (the measured vapor pressure) as a function of time above a solution of 0.01% potassium hydroxide in I at $152.6 \pm 0.1^\circ$ for experiment No. VT-20. An inverted S-shaped curve was obtained. The final pressure reading corresponds to an equilibrium state. In order to demonstrate this more directly, the polymerized I was cooled to room temperature and pumped out thoroughly on a high vacuum system in order to remove all the volatile materials. The system was then returned to the high temperature thermostat and the pressure gradually rose to values very near the final pressure in the original polymerization experiment. In general, the final pressure represented about 0.06 to 0.07 volume fraction of I at all temperatures (see below for the method calculating volume fraction of I from relative pressure reading).

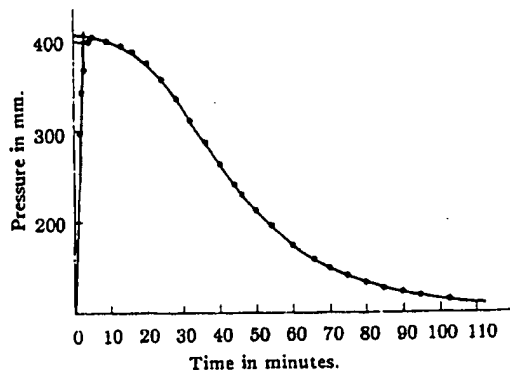


Fig. 1.—Vapor pressure (mm.) as a function of polymerization time, at 152.6° , 0.01% potassium hydroxide.

The vapor pressure of the system decreased from a maximum value close to the vapor pressure of I itself (vapor pressure of I at $152.6^\circ = 407.0$ mm.).⁶ Since P_0 appears in all calculations, its exact evaluation assumed considerable importance. Fortunately, a good linear extrapolation was obtained by plotting pressure against the square of the time. This plot was linear over the initial 15-minute interval in experiment VT-20. Zero time has been arbitrarily set at the time of immersion of the isoteniscope into the thermostat. Approximate pressure readings on the initial rising part of the curve (Fig. 1) are roughly linear. The steep line when extended intersects the P vs. the square of the time line at about 2.7 minutes in experiment No. VT-20. The authors have arbitrarily taken one-half of this time interval as the zero time correction. Thus, P_0 was obtained from the value of the pressure at about 1.3 minutes on the linear pressure vs. the square of the time.

The value of P_0 calculated in this way is then used to obtain P/P_0 and $(1 - \phi_0)$ by the use of Table VI. A typical plot of $(1 - \phi_0)$ vs. time is presented in Fig. 2. It is very evident that the accuracy of determining $(1 - \phi_0)$ is quite poor at low conversions.

Fortunately, the dependence of ϕ_0 as determined by measurements of vapor pressure upon time follows a simple rate expression derived as follows.

(21) A. Smith and A. W. C. Menzies, *THIS JOURNAL*, **23**, 1412 (1910).

(22) H. S. Booth and H. S. Halbedel, *ibid.*, **28**, 2652 (1940).

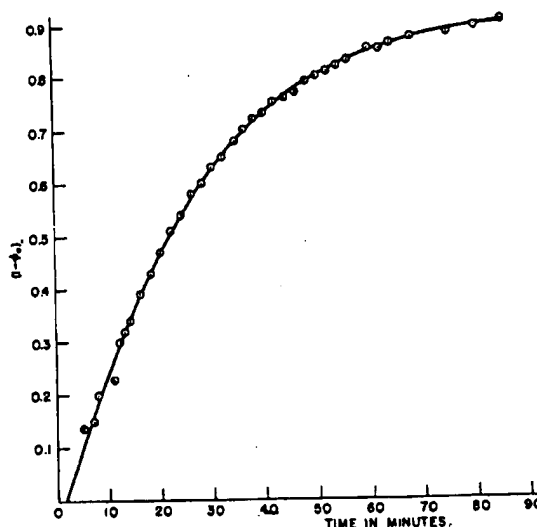


Fig. 2.—Volume fraction of polymer $(1 - \phi_0)$ as a function of time at 152.6° , 0.01% potassium hydroxide.

If I polymerizes at a rate proportional to its volume fraction

$$\frac{d\phi_0'}{dt} = -k\phi_0 \quad (3)$$

where ϕ_0' is the apparent volume fraction of I at time t determined by the polymerization reaction alone and also I is reformed at a rate proportional to the volume fraction of polymer.

$$\frac{d\phi_0''}{dt} = +k'(1 - \phi_0) \quad (4)$$

where ϕ_0'' is the apparent volume fraction of I at time t determined by the depolymerization reaction alone. Combining equations 3 and 4, the net rate of reaction of I becomes

$$\frac{d\phi_0}{dt} = -k\phi_0 + k'(1 - \phi_0) \quad (5)$$

where $\phi_0 = \phi_0' + \phi_0''$. It is apparent that at equilibrium, when $\phi_0 = 0.06$, $d\phi_0/dt = 0$, and hence $k'/k = 0.06$. The rate equation in its integrated form then becomes

$$\ln [\phi_0 - 0.06(1 - \phi_0)] = -kt \quad (6)$$

A plot of $\log [\phi_0 - 0.06(1 - \phi_0)]$ vs. time for the data of experiment No. VT-20 is shown in Fig. 3. A linear relation is found to exist at least up to 80% conversion of I and this substantiates the postulated rate expression. The constant k is expected to vary as temperature, catalyst and catalyst concentration are varied, and this presents a convenient measure of the rate of polymerization of I under a variety of conditions. The rate constant of k has been evaluated by plotting equation 6, above, from the experimental results and determining the slope graphically. Equation 6 always gave good straight lines such that determination of k was a simple matter. (It was of course necessary to convert the slope determined with common logarithms to that value of k appropriate to equation 6 in terms of natural logarithms.)

Results

The Effect of Temperature upon the Rate of Polymerization.—The system I plus 0.01% KOH reacted at various temperatures and the k of equation 6 was evaluated using the methods described above. The temperature dependence of k was then used to evaluate the over-all activation energy for the polymerization reaction. The val-

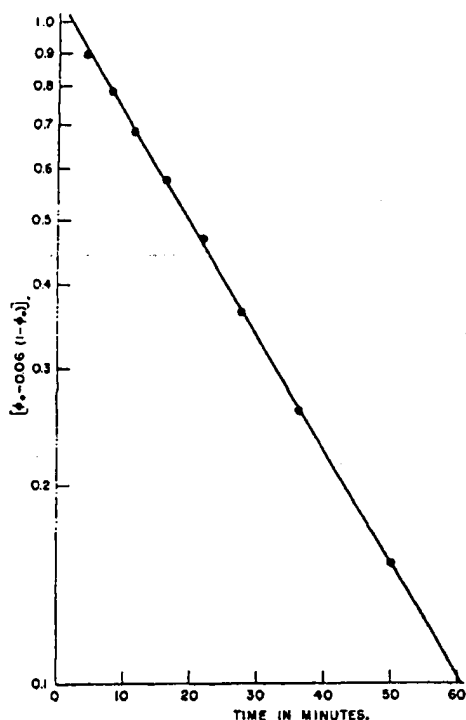


Fig. 3.— $\log [\phi_0 - 0.06 (1 - \phi_0)]$ as a function of time of polymerization at 152.6°, 0.01% potassium hydroxide.

ues of k at various temperatures are presented in Table VII.

TABLE VII

THE RATE CONSTANT, k , AT VARIOUS TEMPERATURES			
Temp., °C.	k (min. ⁻¹)	Temp., °C.	k (min. ⁻¹)
103	0.005	140.0	0.017
102	.059	140.0	.021
152.6	.041	123.6	.0076
152.6	.039	123.6	.0072
140.0	.019		

The relation between k and temperature is found by the method of least squares to be

$$\log k = 8.3042 - \frac{4291.1}{T} \quad (7)$$

where T is the absolute temperature. From this equation, the over-all activation energy of the polymerization reaction is found to be 19.6 ± 1.0 kcal. mole⁻¹. The experimental values of k and a plot of equation 7 are presented in Fig. 4.

The Variation of the Polymerization Rate with Catalyst Concentration.—The temperature dependence of the rate of the polymerization reaction was determined at a single potassium hydroxide concentration, 0.01% by weight (1.78×10^{-3} molar). It was of considerable interest to determine the effect of catalyst concentration upon the rate at a single temperature. The temperature 152.6° was convenient for these measurements.

The rate constant, k was determined by means of equation 6. This quantity increased in a regu-

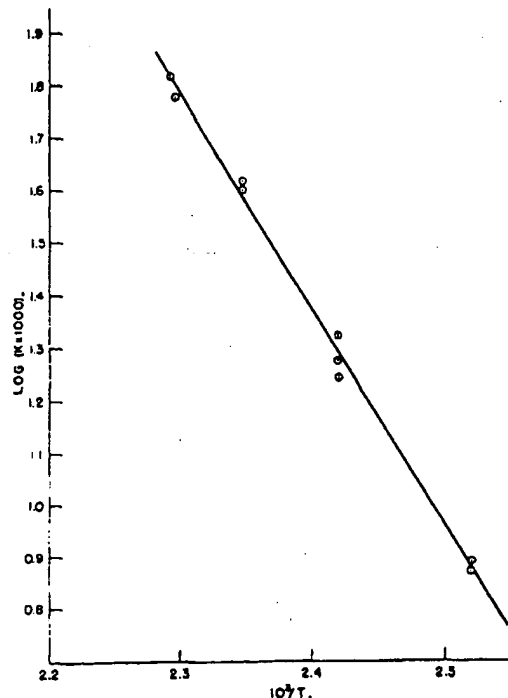


Fig. 4.—Activation energy plot for the polymerization of octamethylcyclotetrasiloxane (I) with 0.01% potassium hydroxide.

lar manner with increasing concentration of catalyst, but was not directly proportional to the catalyst concentration. The values of k at various potassium hydroxide concentrations are presented in Table VIII. It is observed that k is proportional to the square root of the catalyst concentration (Fig. 5). Furthermore, the best straight line through the experimental values of k passes through the origin, indicating that no polymerization takes place at 152.6° in the absence of a catalyst. In order to confirm this prediction, a separate experiment was carried out in which I was heated to 152.6° for 24 hours. During this time, no change in the vapor pressure of the system was observed.

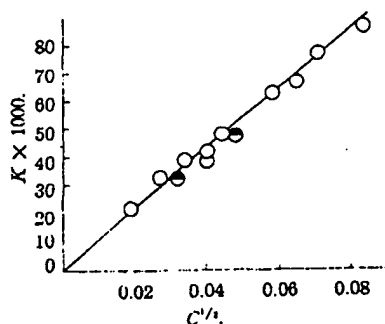


Fig. 5.—The polymerization rate constant k , vs. the square root of the molar catalyst concentration: O, potassium hydroxide; ●, potassium silanolate.

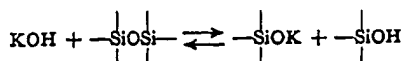
TABLE VIII
THE RATE CONSTANT, k , AS A FUNCTION OF THE CATALYST
CONCENTRATION

Rate constant <i>k</i> (min. ⁻¹)	Potassium hydroxide concn.		
	In weight, %	Molal, <i>c</i>	<i>c</i> ^{1/2}
0.021	0.0022	0.39×10^{-3}	1.98×10^{-2}
.032	.0044	0.78×10^{-3}	2.8×10^{-2}
.038	.0071	1.26×10^{-3}	3.5×10^{-2}
.041	.010	1.78×10^{-3}	4.2×10^{-2}
.039	.010	1.78×10^{-3}	4.2×10^{-2}
.047	.013	2.3×10^{-3}	4.8×10^{-2}
.0625	.021	3.7×10^{-3}	6.1×10^{-2}
.066	.026	4.6×10^{-3}	6.8×10^{-2}
.076	.031	5.5×10^{-3}	7.4×10^{-2}
.086	.043	7.65×10^{-3}	8.7×10^{-2}

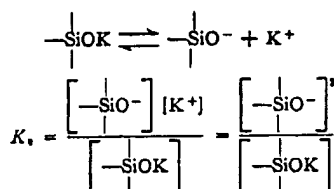
It was of interest to determine the rate of the polymerization using a potassium silanolate salt as the catalyst. The rate constant at two concentrations of potassium silanolate are shown in the plot of Fig. 5 as half shaded circles. It is apparent that the rate is approximately the same whether potassium hydroxide or the silanolate salt is the catalyst.

Discussion

The results just presented strongly indicate that potassium hydroxide reacts with siloxane bonds to form potassium silanolate groups as



The near equivalence of potassium hydroxide and potassium silanolate as catalysts indicate that the above reaction is strongly shifted to the right. It will be observed that starting with the silanolate salt, the reverse of the above reaction cannot proceed if water is not present (to react either directly with the silanolate or to form silanols by reaction with siloxane bonds). Assuming that silanolate is formed essentially quantitatively when potassium hydroxide is added to a siloxane at high temperatures, the following mechanism explains the square root dependence of the rate constant upon the catalyst concentration. Assume that the potassium silanolate is partially ionized to form silanolate anions, which are the active polymerization species. This leads to the equilibrium



where K_0 is undoubtedly very small in the non-polar siloxane medium. We may therefore write

$$[-\text{SiO}-] = \sqrt{K_s} [-\text{SiOK}] = \sqrt{K_s [\text{KOH}]_{\text{added}}}$$

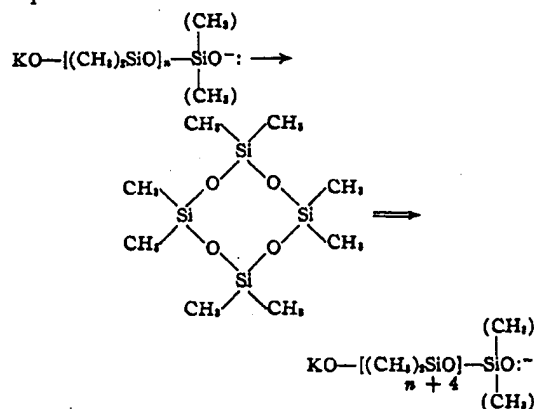
and the rate constant

$$k = A\sqrt{[\text{KOH}]_{\text{added}}} \quad (8)$$

where A may be a function of the temperature and of other conditions. The value of 19.6 kcal./mole found for the over-all activation energy thus contains the temperature dependence of A in equation 7 and is not a true activation energy.

Previous work¹ has shown that the order of reactivity of alkali metal hydroxides as catalysts for the polymerization of I increases in the order potassium, rubidium, cesium hydroxide. The present results suggests that this represents the order of increasing ionization of the corresponding silanolate salts in a siloxane medium. In general, the addition of polar solvents to increase this ionization should result in more rapid polymerization rates.

Previous results have shown that the reaction of organosilicon molecules with electron donors probably takes place by means of a coordinate bond to the silicon atom in the transition state.^{4,7} Thus the propagation step in the polymerization of I may be represented as



The growth of a chain might be halted by a deionization of the silanolate ion (reaction with a potassium ion) or reinitiated by the reionization of the potassium silanolate. In this manner the polymerization continues until an equilibrium concentration of about 6% by volume of I is present. This value for the equilibrium concentration of tetramer agrees well with that calculated from semi-theoretical considerations by Scott.¹⁴

Acknowledgment.—The authors are indebted to Dr. F. R. Mayo for several helpful discussions during the course of this investigation, and special thanks are due to E. M. Hadsell of this Laboratory for carrying out the many analytical distillations.

SCHENECTADY, N. Y.

FULL TEXT OF CASES (USPQ FIRST SERIES)

In re Oda, Fujii, Moriga, and Higaki, 170 USPQ 268 (CCPA 1971)

In re Oda, Fujii, Moriga, and Higaki, 170 USPQ 268 (CCPA 1971)

In re Oda, Fujii, Moriga, and Higaki

(CCPA)

170 USPQ 268

Decided July 1, 1971

No. 8466

U.S. Court of Customs and Patent Appeals

Headnotes

PATENTS

1. Reissue -- In general (§ 58.1)

Reissue statute is based on fundamental principles of equity and fairness; as a remedial provision, intended to bail applicants out of difficult situations into which they get without any deceptive intention, it should be liberally construed so as to carry out its purpose to the end that justice may be done to both patentees and public.

2. Amendments to patent application -- New matter (§ 13.5)

Words and phrases (§ 70.)

"New matter" is a technical legal term in patent law, a term of art; its meaning cannot be clearly defined; term is on a par with such terms as "infringement," "obviousness," "priority," "abandonment," and the like which express ultimate legal conclusions and are in the nature of labels attached to results after they have been reached by processes of reasoning grounded on analyses of factual situations; court must decide on a case-by-case basis what changes are prohibited as "new matter."

3. Amendments to patent application -- New matter (§ 13.5)

In a sense, anything inserted in specification that was not there before is new to the specification but that does not necessarily mean that it is prohibited as "new matter."

4. Reissue -- Same invention as original (§ 58.7)

Reissue must not change invention described in original patent.

5. Amendments to patent application -- New matter __ (§ 13.5)

One skilled in the art would appreciate not only existence of error in specification but what the error is; as a corollary, it follows that when nature of this error is known it is also known how to correct it; hence, change of wording to correct error is not "new matter."

6. Reissue -- Inadvertence, accident and mistake __ (§ 58.3)

There is nothing in 35 U.S.C. 251, pertaining to reissue of defective patent which resulted from "error without any deceptive intention," as to timeliness of applicant's actions in prosecution of application for original patent nor is there any prohibition of reissue on ground that applicant or his attorney knew of error at time original patent issued.

7. Amendments to patent application -- New matter __ (§ 13.5)

Specification -- Sufficiency of disclosure __ (§ 62.7)

Fact that a change deprives phrase of a needed antecedent so that a reader might be somewhat confused does not result in injection into specification of prohibited "new matter" within meaning of 35 U.S.C. 251; it may give rise to need for rewriting or clarification and be ground for rejection under first paragraph of section 112, but "new matter" rejection because of that defect is unwarranted.

Particular patents--Compounds

3,244,730, Oda, Fujii, Moriga, and Higaki, Phthalides Compounds, claims 1 to 3 of reissue application allowed.

Case History and Disposition:

Page 268

Appeal from Board of Appeals of the Patent Office.

Application, Serial No. 574,260, filed Aug. 5, 1966, of Ryohei Oda, Hiroshi Fujii, Hiroyuki Moriga, and Taiji Higaki, for reissue of Patent No. 3,244,730, issued Apr. 5, 1966; Patent Office Group 120. From decision rejecting claims 1 to 3, applicants appeal. Reversed.

Page 269

Attorneys:

Arnold G. Gulko, Washington, D. C., for appellants.

S. Wm. Cochran (R. E. Martin of counsel) for Commissioner of Patents.

Judge:

Before Rich, Almond, Baldwin, and Lane, Associate Judges, and Re, Judge, United States Customs Court, sitting by designation.

Opinion Text**Opinion By:**

Rich, Judge.

This is a reissue case involving only questions of law as to compliance with 35 U.S.C. 251. Patentability of the subject matter of the appealed claims, which are directed to chemical compounds, with respect to novelty, unobviousness, and utility, is not in issue. This appeal is from the decision of the Patent Office Board of Appeals affirming the rejection of claims 1-3 of application serial No. 574,260, filed August 5, 1966, to reissue patent No. 3,244,730, granted April 5, 1966, on application filed July 17, 1963. We reverse.

The Invention

The invention sufficiently appears from the appealed claims:

1. 5-nitro-3, 3-bis- (4-dimethylaminophenyl)-phthalide.
2. 5-acetylamino-3, 3-bis- (4- dimethylaminophenyl)-phthalide.
3. 5-benzoylamine-3, 3-bis- (4- dimethylaminophenyl)-phthalide.

The above phthalides are said to be useful as intermediates for conversion into basic dyes and also in pressure-sensitive copying papers of known construction because they are reactive with acidic clays to form a color.

The application for the original patent was prepared by translation into English from corresponding Japanese applications filed in May 1960 and July 1962, which are identified in the reissue oath. The oath points out that in the translation certain errors were made which are discussed in more detail later. The most important error was that "nitric acid" was mistranslated "nitrous acid." Of less importance, "ferrous oxide" in the U. S. application should have been "iron."

These errors were known to applicants' U.S. attorney before the patent issued. He thought he would be able to have them corrected, before the patent issued, by an amendment under Patent Office Rule 312, pertaining to amendments after allowance, which he filed February 2, 1966, but the examiners recommended against and refused entry. Four months after the issuance of the patent containing the translation errors, which were thought to affect its validity and therefore its adequacy to protect the compounds of the above claims by reason of an insufficient or inaccurate description of how to make them, under the first paragraph of 35 U.S.C. 112, this application for reissue was filed.

The Rejection

As background for understanding the rejection we set forth the text of 35 U.S.C. 251, first paragraph, the rest of the section being irrelevant here (added emphasis ours):

§ 251. Reissue of defective patents

Whenever any patent is, through error without any deceptive intention, deemed wholly or partly *inoperative or invalid*, by reason of a *defective specification* or drawing, or by reason of the patentee claiming more or less than he had a right to claim in the patent, the Commissioner shall, on the surrender of such patent and the payment of the fee required by law, reissue the patent *for the invention disclosed in the original patent*, and in accordance with a new and *amended* application, for the unexpired part of the term of the original patent. *No new matter* shall be introduced into the application for reissue.

The posture of the case on appeal, so far as amendments to the specification are concerned, is that in three instances in the descriptive portion of the specification, including a specific example, the word "nitrous" is changed to "nitric" and in Example 2 the words "ferrous oxide" were first changed to "iron" and then to "reducing agent." ¹ Additionally, three process claims (4-6) which contained references to "nitrous acid" have been cancelled or deleted from the patent.

The Examiner's Answer states:

Claims 1-3 stand rejected as being based on a specification containing new matter. 35 U.S.C. 251; 35 U.S.C. 112. The changes of "nitrous" to "nitric" and "ferrous oxide" to "iron" to "reducing agent" are deemed to be drawn to new matter. The specification is considered defective since without the introduction of new matter, the specification is drawn to inoperative embodiments. Applicants are not permitted to add new matter in order to disclose what they intended even though it can be shown that it was part of the original invention and had been inadvertently omitted from the original specification. The fact that the original specification is at variance with the Japanese application * * * does not provide the proper basis for such a correction. Ex parte Bondiou et al., 132 USPQ 356 [Pat.

Page 270

Off. Bd. App. 1961]. Since both nitrous acid and nitric acid are known to effect the nitration process, the error would not be considered obvious by one of ordinary skill in the art.

This rejection can also be construed as being based on a defective oath. The oath should state facts and not conclusions or opinions. Applicants' oath, e.g., at page 2, line 1, in referring to the errors in translation as "obvious", fails to comply with these requirements. M.P.E.P. 1401.08; Ex parte Pfaudler, 1883 C.D. 1, 23 O.G. 269; Ex parte Timkin, 1883 C.D. 58, 24 O.G. 1089.

In affirming, the board first pointed out that the appealed claims correspond "exactly to the identically numbered claims of appellants' original patent," thus making it clear that there will be no change whatever in the invention claimed by virtue of reissue, if permitted. The board pointed out that the whole controversy revolves around the section 251 provisions relating to "error without any deceptive intention" and "new matter." With an extensive effort to deflate all of appellants' arguments to the contrary, the board held that the change of "nitrous" to "nitric" would be "new matter."

The board next took up the question of "error" under section 251, a question the examiner had not raised at all. Indeed, the Examiner's Answer appears throughout to assume there was error and nothing was said about deceptive intention. The board, however, seemingly sua sponte, made a new approach to the question of whether there was "error without any deceptive intention" and reached the conclusion that "appellants' showing of 'error' under 35 U.S.C. 251 must be held to be insufficient." This new holding seems to have been based not on the *absence* of error but on appellants' attorney's handling of the prosecution--his "course of action"--in permitting the patent to issue, knowing of the errors in it, and in the time he took for various matters, such as discussing the errors with another attorney and getting information from Japan and from a local expert. Frankly, we do not follow the board's reasoning on this

point.

Finally the board took up the other question of whether the changes involving the "ferrous oxide" amounted to insertion of "new matter." The board disagreed with the examiner in considerable part in finding that the simple deletion of the words was not in violation of section 251. It said:

No new matter would be involved in the cancellation, and the term "reducing agents" is found in the original application. Moreover, the record does not reveal that the error in "ferrous oxide" was known as early as the error in "nitrous acid."

It nevertheless found "a new matter aspect" in the changes made because the deletion of "ferrous oxide" from Example 2 and its replacement by "reducing agent" would cause the example to be somewhat confusing. On this point, therefore, the "new matter" issue would seem to be converted into the question whether the creation of confusion or ambiguity by a change in a specification constitutes a violation of the prohibition against "new matter."

Opinion

[1] This court on previous occasions, particularly since the effective date of the 1952 Patent Act, has observed that the reissue statute is based on fundamental principles of equity and fairness and that, as a remedial provision, intended to bail applicants out of difficult situations into which they get "without any deceptive intention," it should be liberally construed so as to carry out its purpose to the end that justice may be done to both patentees and the public. In *re Willingham*, 48 CCPA 727, 282 F.2d 353, 127 USPQ 211 (1960); In *re Wesseler*, 54 CCPA 735, 367 F.2d 838, 151 USPQ 339 (1966). Both of these cases were cited with approval, for the proposition we have stated, in *Reeves Bros., Inc. v. U. S. Laminating Corp.*, 282 F.Supp. 118, 127, 157 USPQ 235, 243 (E.D. N.Y. 1968). At the same time we are realistic enough to appreciate that sharp applicants must be watched with a sharp eye. This is nothing new in the legal field.

[2] The problem here is whether the changes appellants wish to make constitute "new matter" within the meaning of section 251. ² "New matter" is a technical legal term in patent law--a term of art. Its meaning has never been clearly defined for it cannot be. The term is on a par with such terms as infringement, obviousness, priority, abandonment, and the like which express ultimate legal conclusions and are in the nature of labels attached to results after they have been reached by processes of reasoning grounded on analyses of factual situations. In other words, the statute gives us no help in determining what is or is not "new matter." We have to decide on a case-by-case basis what

Page 271

changes are prohibited as "new matter" and what changes are not.

[3] In a sense, anything inserted in a specification that was not there before is new to the specification but that does not necessarily mean it is prohibited as "new matter."

Robinson On Patents (1890), § 561, in discussing amendment of applications, says:

No new matter can under any circumstances be introduced by amendment. New matter is that which is not found in the specification, drawings, or model, as first filed, *and which involves a departure from the original invention.* [Emphasis ours.]

In the chapter on reissues, Walker on Patents, first Deller's Edition (1937), § 311 New Matter, says: ³

The provision, first enacted in The Patent Act of 1870 * * * that "no new matter shall be

introduced into the specification" is merely another way of saying that a reissued patent shall be for the same invention as the original. * * * That provision, therefore, neither enlarged nor restricted the reissuability of Letters Patent; and, accordingly, it is not new matter, within its meaning, to state a new use of the invention shown in the original * * * nor to explain, in a reissue, the operation of a device which in the original was only described * * * nor to vary the description of anything described in the original.

Of course, these generalities are not the whole story and leave many unanswered questions.

Rivise and Caesar, in *Patentability and Validity* (1936), in a discussion of former Patent Office Rule 70, which is now Rule 118, say, in § 248:

This rule is known as "the rule against new matter" and is intended to prevent an applicant under the guise of an amendment from introducing into his application *a wholly different invention or changing the construction of a fully disclosed invention or presenting a different or preferred form of the invention*. The applicant must stand or fall on his original disclosure and all amendments must conform thereto. This rule appears very simple but patent tribunals have experienced considerable difficulty in interpreting and applying it in practice. [Emphasis ours.]

The authors then proceed to list 14 categories into which they have put the adjudicated cases, the first of which is

1. Amendments purporting to correct errors or supply omissions in features which are essential to the completeness of the disclosure.

This point they then discuss for four pages in § 249 from which we extract the following (all emphasis ours):

Amendments purporting *to correct errors* or to supply omissions in features which are essential to the *operativeness* of the invention or the completeness of the disclosure *are permissible, if the errors are manifest* and were caused by a clerical mistake of the draftsman or unfamiliarity of the inventor with official forms *and the proposed corrections do not change the essence of the invention*. * * *

If the changes necessary to make the disclosed device operative are *radical* in their nature and constitute a *departure from the invention originally disclosed*, they are not permissible.

A case discussed at great length in the above section is an interference decided by this court, *Quigley v. Zimmerman*, 22 CCPA 713, 73 F.2d 499, 23 USPQ 310, 314 (1934), wherein, in the course of discussing a "new matter" problem, the court said (emphasis ours):

That amendments may be made to patent applications for the purpose of *curing defects, obvious to one skilled in the art*, in the drawings or written descriptions of inventions, is so well settled that we deem it unnecessary to cite authorities in support thereof.

With this general background on the law, admittedly sketchy, we turn to the specific problems before us in this case. The first question is whether, under all the circumstances, the changing of "nitrous" to "nitric" involves "new matter."

[4]Running through the foregoing discussion of the law is the clear and basic concept that *the invention* described in the original patent must not be changed. We note, first of all, that that is not a problem in this case. The invention before us, as defined in the claims, consists of three specific chemical compounds. There is no change proposed in the claims or in the description of the claimed compounds

in the specification. There is no deviation whatever with respect to the invention.

The change from nitrous to nitric acid occurs only in description of how to make the claimed compounds, which is not the invention since no process is now claimed. In the principal illustrative example (wherein two of

Page 272

the three occurrences of "nitrous" appear), Example 1, is the following key passage (emphasis added):

A liquid mixture (5.5 ml.) of sulfuric acid (specific gravity 1.80) and *nitrous acid (specific gravity 1.45)* having a ratio of sulfuric acid to *nitrous* acid of 5:1 is gradually added to the solution of phthalide compound in sulfuric acid and the mixture so produced is maintained at a temperature in the range of from 0-30°C. for one hour.

This is part of the description of a nitrating process which the record in this case shows to be a well-known reaction.

Appellants have produced affidavit evidence from an apparently well-qualified chemist, Dr. Zisman, for 10 years prior to making his 1966 affidavit Superintendent of the Chemistry Division of the U. S. Naval Research Laboratory, showing that the passage italicized above is obviously in error. Obviousness is predicated on the fact that nitrous acid cannot exist at a specific gravity of 1.45 because the solubility in water of nitrous oxide is so low that it is not feasible to provide nitrous ⁴acid at specific gravities in excess of approximately 1.023, thus making the existence of error apparent on the face of the patent.

Either the term "nitrous acid" is wrong or the specific gravity is wrong. The Patent Office contends that there is no way of telling which it is, but appellants submit several good reasons in support of their contention that one skilled in the art would know that it is the acid that is misnamed. We think appellants have the better of the argument. The Patent Office sets up the number of occurrences of "nitrous"--six, counting the three original process claims no longer in the case--as against the single occurrence of the numeral and says mistakes in numerals are very common. We do not find this numerical argument weighty. Once the translator decided, incorrectly, that what the Japanese application said was "nitrous" it was only reasonable that he should be consistent; we are considering a translation error, not a typographical error. Appellants make four points based on the Zisman affidavit as to why a skilled chemist would assume that nitric acid was meant: (1) A specific gravity of 1.45 is correct for concentrated nitric acid, the evidence being that it would represent 79.5% HNO₃; (2) nitric acid is the acid normally used in admixture with sulfuric acid for nitrating; (3) nitrous acid is known not to be desirable for the nitration of amine, and amines are here being nitrated; (4) even if nitrous acid were used it would be generated in situ because of its instability in aqueous solution, but that is not how the nitration process is described in the patent. In addition to and on the basis of these reasons, Dr. Zisman expressed his judgment as a chemist that it was clear to him that nitric acid was intended. There appears to be a fifth reason brought out in argument, namely, that specific gravity is an inappropriate way of identifying the concentration of nitrous acid in water because its maximum specific gravity of 1.023 is too close to that of water, which is

[5]1.000. On all the evidence, we conclude that one skilled in the art would appreciate not only the existence of error in the specification but what the error is. As a corollary, it follows that when the nature of this error is known it is also known how to correct it. We therefore disagree with the board's first conclusion that the change of "nitrous" to "nitric" is "new matter."

We also think there is adequate evidence in the record to show that the error in saying "nitrous" instead of "nitric" was a translation error. The reissue oath, made by all four inventors, so states. A separate

affidavit of Hiroshi Fujii, one of the inventors, familiar with the U. S. application and the corresponding Japanese application, states that in the Japanese application "the word 'nitric' [in Japanese, presumably] is used at each place" where the word "nitrous" appears in the U. S. application and that the error was due to faulty translation of the Japanese into English. Beside that, all of the circumstances of the case as shown by correspondence introduced with the affidavit of Arnold G. Gulko, the U. S. attorney, point to the existence of a translation error which was discovered by the inventors during the prosecution. The Patent Office complains that there is no certified copy of the Japanese application on file and no sworn translation. While no doubt the best evidence of translation error would be, in part, a copy of the Japanese application or patent, its absence is not fatal since we find the evidence of record sufficient. There is not the slightest evidence to cast doubt on appellants' assertions or any suggestion they are trying to change the nature of the invention patented.

The board's second point is that there has been no "error without any deceptive intention." As stated above, this was not a ground of rejection put forward by the examiner. The Patent Office brief admits the board raised the question on its own. We have read the board's

Page 273

argument with care and still are not clear as to the basis on which it found no "error." Its finding seems to be based on a mixture of two things: the amount of *time* the attorney took to carry out various aspects of the prosecution after he became aware of the error and that he *knew* there was error in the patent when he allowed it to issue. What happened was that after becoming aware of the error an attempt was made to correct it by amendment filed February 2, 1966, under Rule 312 (Amendments after allowance). Entry of the amendment was refused on February 14 and the patent issued on April 5, 1966. Recourse was then had to this reissue application, filed August 5, 1966.

[6]What the 1952 statute says is that when the patent is deemed "inoperative or invalid"--i.e., it is ineffective to protect the invention adequately or it is a nullity--and it is so because of *error*, and the applicant for reissue is not guilty of "any deceptive intention," then the patent may be reissued, subject to the other provisions of the statute. We are unable to find in this provision anything pertaining to the timeliness of an applicant's actions ⁵in the prosecution of the application for the original patent. Neither do we find any prohibition of reissue on the ground the applicant or his attorney knew of the error at the time the original patent issued. The board seems to have premised its ruling on this point primarily on *Ex parte Zihlerl*, 116 USPQ 162 (Pat. Off. Bd. App. 1957). Although that case was decided after the 1952 Patent Act, the opinion makes it clear that the term "error" therein was equated with the term "inadvertence, accident or mistake" of the prior statute, R.S. 4916, former 35 U.S.C. 64. In *Wesseler*, supra, we ruled that the 1952 reissue statute broadened the term "error" by not limiting it to "error" that had arisen through "inadvertence, accident, or mistake." *Wesseler* was subsequent to *Zihlerl*. Cases relying on the language of the former statute are no longer controlling. To "equate" the language of the present statute with that of the old statute, as was done in the *Zihlerl* opinion, is to ignore the change that Congress made and to deny to applicants the benefit of the intentional broadening. Nothing the board has said persuades us that this is not a case of "error without any deceptive intention." In fact, the record as a whole presents a picture of prosecution conducted in complete good faith. ⁶

The board's final point brings us back to an attempt to rectify another translation error and as in the other case we have the reissue oath and a second Fujii affidavit as evidence establishing the existence of error due to faulty translation. In two places the specification mentions "ferrous oxide," which served in the process of making the claimed compounds as a reducing agent. The specification says it is a reducing agent and names others. The oath and affidavit say the correct translation should have been "iron" rather than "ferrous oxide." The reissue sought to make this change, but after filing, by amendment, appellants deleted both references to "iron" and in Example 2 inserted in its place "reducing agent." The board partially reversed the examiner in saying that the *deletions* did not result in "new matter." However, the

board found that, with the change, Example 2 "would be confusing" for lack of an antecedent for the expression "essentially free of ferric hydroxide contamination." It deemed this "a new matter aspect" and said:

To the limited extent indicated by the foregoing discussion, the holding of new matter in Example 2 will be sustained.

[7] We do not agree with the "new matter" rejection under these circumstances. The mere fact that a change deprives a phrase of a needed antecedent so that a reader might be somewhat perplexed or confused does not result in the injection into a specification of prohibited "new matter" within the meaning of § 251. It may give rise to a need for rewriting or clarification and be ground for a rejection under § 112, first paragraph, but a "new matter" rejection because of that defect is unwarranted.

Since we disagree with the board on each of the three grounds on which it sustained the rejection, its decision is *reversed*.

Footnotes

Footnote 1. At another point appellants deleted by amendment the words "ferrous oxide and," after first changing "ferrous oxide" to "iron."

Footnote 2. The same term appears in 35 U.S.C. 132 permitting applications for original patents to be amended. It provides that "No amendment shall introduce new matter into the disclosure of the invention." Presumably, and we believe desirably, the same term would and should have the same meaning in both contexts.

Footnote 3. Deller's Second Edition, § 304, is the same except for a reference to the 1952 Patent Act's prohibition of new matter in § 251.

Footnote 4. As an illustration of how human it is to err, we take note of an error in this Zisman affidavit where he used the word "nitric" at this crucial point in the affidavit although the context makes it perfectly clear that he meant to say "nitrous." No one appears to contest that that was the intention.

Footnote 5. The only provision in § 251 relating to time is the last paragraph which provides that a reissue "enlarging the scope of the claims" must be applied for within two years from the patent grant.

Footnote 6. The Patent Office appears to admit that it was. A footnote to the Solicitor's brief says:

The record shows that appellants are not charged with "any deceptive intention", as that expression is used in Section 251.

- End of Case -

Contact customer relations at: customer care@bna.com or 1-800-372-1033

ISSN 1526-8535

Copyright © 2006, The Bureau of National Affairs, Inc.

[Copyright FAQs](#) | [Internet Privacy Policy](#) | [BNA Accessibility Statement](#) | [License](#)

Reproduction or redistribution, in whole or in part, and in any form, without express written permission, is prohibited except as permitted by the BNA Copyright Policy. <http://www.bna.com/corp/index.html#V>

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.